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(54) Fused Alumina-zirconia  
Abrasive Product

(57) An abrasive grain comprises (i) 27 to 35% by weight of zirconia, (ii) titanium dioxide or a reduced form thereof in an amount on analysis expressed as the oxide of 1 to 10% by weight, (iii) impurities, if any, in a total amount on analysis expressed as the oxides of not greater than 3% by

weight, and (iv) a balance of alumina. The microstructure of the abrasive grain comprises primary alumina crystals embedded in a supporting alumina-zirconia eutectic matrix. The grain may be produced by solidifying a melt of suitable composition in under three minutes by means of a suitable heat sink material.

The abrasive grain may be used to produce coated abrasive products or bonded abrasive products.

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## SPECIFICATION

## Fused Alumina-zirconia Abrasive Product

The present invention relates to an abrasive grain, to a method of producing such grain, and to abrasive products incorporating such grain.

5 Abrasives based on substantially pure alumina or alumina modified with 0.25% to 6% additions of minor impurity phases, or residual impurity phases derived from the original starting materials, have proved to be the most versatile and commercially important abrasive systems. They find application in the most diverse types of grinding operation involving the more common types of metal.

10 Although the levels of impurity are quite low their influence on the abrasives' grinding performance can be most dramatic and significant. By changing the impurities, cooling and solidification rate of the fused mass of material, a range of "alumina abrasives" has been developed over the years. The individual types have unique combinations of properties, e.g. Hardness, Toughness, Frictional Characteristics, Microstructure, Fracture Properties, Thermal Behaviour, etc., which have made each type ideally suited to a specific area of field of grinding applications using Coated and Bonded Abrasive products containing them.

15 Until recently no commercially competitive material has been available which offered grinding properties superior to those of substantially pure aluminas, particularly in applications where the contact pressures were low to moderate.

20 Attempts have been made to alloy alumina with other oxides at much higher levels than had previously been used. The material showing distinct promise of success was zirconia.

Such attempts met with some success when at least 10% by weight of zirconia was fused with aluminium oxide and when the fused zirconia-alumina mixture was rapidly solidified.

25 U.S. Patent 3,156,545 to Kistler et al discloses that an abrasive having a grinding removal rate comparable to the removal rate of alumina can be prepared by rapidly cooling a composition containing about 15% to 60% by volume of glass, such as silicon dioxide, to form a glassy matrix in which particles of zirconia and alumina are embedded. The resulting abrasive, however, was not substantially superior to alumina in steel removal rate.

30 Other alumina-zirconia alloys have, however, been disclosed in subsequent U.S. and British Patents wherein high purity alumina and zirconia are used. The products disclosed in these patents do show substantial improvements in performance, in specific areas, over alumina.

35 For example U.S. Patent 3,181,939 to Marshall and Roschuk discloses that high strength abrasives can be obtained when from 10 to about 60% by weight of zirconia is fused with alpha alumina and the resulting fusion is rapidly cooled. The patent discloses that such abrasives are suitable for steel snagging operations, (i.e. high pressure operations) where high strength is required. The patent, however, indicates that the alpha alumina should be of high purity, usually at least 99.8% by weight aluminium oxide, and further indicates that the purity of the zirconia should be preferably at least 99%.

40 As disclosed in U.S. Patent 3,891,408 to Rowse and Watson and U.S. Patent 3,893,826 to Quinan et al the best grinding and polishing abrasive characteristics are obtained when the proportions of zirconia to alumina are such that a eutectic structure is formed when the fused alumina-zirconia mixture is rapidly cooled.

45 U.S. Patent 3,891,408 to Rowse and Watson teaches the very rapid crystallization of eutectic and near eutectic molten mixes of aluminium oxide and zirconium oxide. They believe the optimum eutectic composition and performance in moderate pressure applications occurs at 43% by weight of zirconia, but in any event the amount of zirconia in their abrasive grain is 35—50% by weight. The zirconium oxide in their material is in the form of rods (or platelets) which, on the average, are less than 3000 angstroms in diameter, and preferably at least 25% by weight of the zirconium oxide is in the tetragonal crystal form. The solidified melt is made up of cells or colonies, typically 40 microns or less across their width. Groups of cells having identical orientation of microstructure form grains which typically include 2 to 100 or more cells or colonies. In crushing the material fractures along grain and cell boundaries. The abrasive grits produced are described as having very high strength combined with highly desirable microfracture properties.

50 The novel and unexpected feature of the abrasives produced in accordance with U.S. Patent No. 3,891,408 was that when produced at or near the eutectic composition they were outstandingly useful in "light duty applications". Abrasive grits produced in accordance with U.S. Patent 3,891,408 gave improvements in excess of 100% of prior art standards when incorporated in Coated Abrasive products and tested in low or moderate pressure applications. When such grits were incorporated into Bonded products substantial improvements were obtained in low to moderate pressure applications.

60 The properties of the abrasive grains produced in accordance with U.S. Patent No. 3,891,408 are to be contrasted with the use of lower zirconia levels, e.g. 25% which leads to very tough abrasives which find utility in high pressure operations such as snagging operations.

It has now been discovered that despite the teaching of U.S. Patent 3,891,408 highly effective alumina zirconia abrasives having low to moderate pressure performance similar to or better than those produced at or near the eutectic composition, can be produced using lower amounts of zirconia

than contemplated in U.S. Patent 3,891,408 by incorporating sufficient titania or a reduced form thereof in the abrasive.

According to a first aspect of the present invention there is provided an abrasive grain comprising 27 to 35% by weight zirconia, titanium dioxide or a reduced form thereof in an amount on analysis expressed as the oxide of 1 to 10% by weight, impurities, if any, in a total amount on analysis expressed as the oxides of not greater than 3% by weight, and a balance of alumina.

According to a second aspect of the invention there is provided a method of producing an abrasive grain as defined in the preceding paragraph from a melt which on solidification gives a grain of the defined composition, wherein the solidification to produce the grain is effected in under three minutes by contacting the melt with a suitable heat sink material.

The present invention also provides abrasive products, for example coated abrasive products or bonded abrasive products which incorporate the abrasive grain of the invention.

The amounts of titania or the reduced form thereof and the amounts of impurities in the abrasive grain of the invention given above are the analyses expressed as oxides. This is conventional practice in abrasive technology but does not mean to say that the titanium or impurities, if any, are necessarily present as oxides and indeed this may well not be the case as will be seen from the following description. Nevertheless, conventional analytical techniques for abrasive products determine, and express, the amounts of the various components as oxides and this practice is adopted herein. In fact, the general procedure is to determine the amounts of the various components, excluding alumina, as oxides, and to express the balance of the composition as being of alumina and it is on this basis that the analytical figures for abrasive grains are quoted herein.

In the following description it is to be understood that references to the amount of titania or reduced form thereof or impurities in the abrasive grain are the analytical figures expressed as oxides.

The amount of titanium dioxide or reduced form thereof (which may for example be a suboxide, oxycarbide or carbide) present in the abrasive grain of the invention is from 1 to 10% by weight, preferably from 1 to 5% by weight. Although such high levels of titanica or reduced form thereof, have been found to be detrimental to the performance, in common grinding operations, of abrasive grains with an approximately eutectic composition of zirconia and alumina, they surprisingly enhance the low to moderate pressure performance of abrasive grains which include 27 to 35% by weight of zirconia. The mechanism by which the titanium dioxide or reduced form thereof provides this improvement of properties is uncertain but may be due to an enhancement of frictional characteristics and rate at which heat is generated when in contact with the metal, which would thermally assist the penetration of the abrasive into the metal.

The impurities, if any, which are present in the grain are either the residual impurities introduced with the starting materials or additions which have deliberately been made. Such additions may have been made, for example, to assist refining, e.g. iron and carbon are added to Bauxite fusions to reduce and control silica and iron oxide levels. It is in fact common practice to add materials to adjust the final analysis or to combine undesirable phases to facilitate their removal by precipitation to the base of the furnace, or volatilisation from the surface of the melt.

Since it is economically not possible to remove all impurities completely, the abrasive grain of the invention may contain certain impurities which can critically effect and can detract from its performance. It is essential that such materials be kept within certain limits. Such materials are alkalis (soda, potash, lithia) alkaline earths, silica and ferric oxide. These may be present individually, in combination with one another, or in combination with the major phases, or exist in reduced forms such as carbides, nitrides or even free metals.

The potency of such detrimental impurities is variable. Alkalis, particularly soda, have a devastatingly detrimental effect on performance. Silica is also detrimental at the zirconia levels used in the present abrasives but is less harmful than alkalis. Alkaline earths are more easily avoided in the final composition but are thought to be similar or less detrimental than silica. It should be noted that at zirconia levels higher than those used in the present invention, for example at the eutectic zirconia alumina composition, silica may in fact be a beneficial ingredient as described for example in U.K. Patent Application No. 79 00550.

Thus in the final composition the level of the other minor impurity phases should be kept to the minimum economic levels. These are dictated by the choice, cost, availability and quality of the sources of alumina and zirconia and the extent to which they can be favourably modified economically by the fusion technique employed. Irrespective of the material sources or the fusion technique imposed the final composition should preferably not contain more than 0.1%  $\text{Na}_2\text{O}$  or more than 1.5%  $\text{SiO}_2$  and preferably below 1%  $\text{SiO}_2$ . At these upper limits of  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  their deleterious effect is not too great and in part can be neutralised by adjusting the Titania levels. Additionally the combined weight percentage of  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  should not exceed 1.5%.

The abrasive grain of the invention may be produced by rapidly solidifying an alumina-zirconia cofusion which additionally includes the required titanium dioxide or reduced form thereof, and possibly also impurities, and which on solidification gives an abrasive grain in accordance with the invention. Solidification is effected by contacting the co-fusion with a heat sink material and should take place in under 3 minutes, more preferably in under 1 minute, most desirably in under 20 seconds.

The heat sink material, or cooling vehicle, may take the form of metallic balls, metallic rods or plates, or lumps of prefused abrasive material, onto which the co-fusion is poured.

One important criteria for the cooling vehicle is that it has a configuration, size and mass that it forms voids or spaces into which, and surfaces onto which, the molten material can gain access. In so doing the cooling vehicle should expose a sufficiently large surface area to the molten mass to achieve solidification of the melt within the specified time of 3 minutes and preferably well below 1 minute of the molten material contacting the surface provided by the cooling vehicle. At the very high rate of heat transfer the cooling vehicle should be capable of absorbing the thermal energy involved without melting or severe deterioration of its properties to enable the cooling vehicle to be used repeatedly. An example of such a cooling vehicle which achieves the above objectives is the Rod Mould as detailed in British Patent Application Number 41763/77. This is simply an example, and other techniques well known in the art may be used.

A further example of cooling method is, instead of pouring the melt into a cooling vehicle, to introduce a cooling vehicle into the melt and to withdraw the cooling vehicle when a layer of product has solidified thereon.

Once separated from the cooling vehicle, the solidified mass may be subjected to the normal types of crushing procedures to produce abrasive grits. The crushing procedure may comprise primary jaw crushing, secondary roll crushing, Canary milling or hammer impact milling. The crushing technique used may be varied to produce grits having different shapes. This is common practice in the industry to extend the use of specific abrasive compositions to as wide an area of abrasive products and applications as possible. For example a more friable weak elongated sharp grit may be required in certain coated abrasive applications whereas a sharp but more "blocky" tougher grain may be required in certain bonded abrasive applications.

The particle size of the abrasive grits produced may be between 6 to 1000 grit as defined by FEPA standards issued 1971/2 or U.S. Department of Commerce Commercial Standard CS271-65 issued April 12 1965. The grit size is preferably between 6 and about 180 and most desirably is between about 14 and 80.

The abrasive grain of the invention may be utilised for the production of coated abrasive products and bonded abrasive products in conventional manner. The inventive abrasive grain may be the sole abrasive in such products, or may be used in conjunction with conventional abrasives.

A more detailed description of the method of producing the abrasive grain will now be given by way of example only.

The alumina for the intended composition may be introduced in the form of Bauxite or Calcined Alumina obtained from the Bayer process or surplus abrasive grits containing a substantial quantity of alumina. Bauxite used in the abrasive industry in addition to alumina usually contains from about 3 to about 4.5 weight percent titania, from about 3 to about 8 weight percent silica, and from about 3 to about 10 weight percent iron oxide ( $\text{Fe}_2\text{O}_3$ ).

The Bauxite may be synthetic bauxite, unpurified calcined bauxite or only partially purified Bauxite, i.e. alumina made by the fusion and reduction of calcined Bauxite with metallic iron and carbon. When unpurified calcined Bauxite is used directly, iron and carbon should be incorporated into the Bauxite-Zirconia fusion to remove iron oxide and as much silica as possible. Titania may also be reduced to too low a level in this system and further additions of Titania may be necessary to adjust the final analysis.

Synthetic bauxite is produced by combining or mixing pure alumina with desirable impurities such as titania which is then used in place of the natural bauxite.

Pure alumina used herein may be surplus abrasive grits high in alumina or calcined alumina obtained from the Bayer process. The latter has two forms which differ in soda content. Low Soda Calcined Alumina containing 0.1% or less  $\text{Na}_2\text{O}$  by weight and Normal Calcined Alumina containing 0.5—0.3%  $\text{Na}_2\text{O}$  by weight.

The zirconia required by the composition is preferably provided in the form of Baddelyite ore which usually contains from:—

about 95 to 99 weight percent zirconia  
about 0.3 to about 3 weight percent silica  
about 0.5 to about 2 weight percent titania  
about 0.5 to about 2 weight percent iron oxide.

Any Hafnia present is inclusive in the weight percent figure quoted for zirconia.

When compared with bauxite, the Baddelyite ore is found to contain lower percentages of silica, titania and iron oxide than unpurified bauxite.

The zirconia may alternatively be provided by zirconia bubbles made by smelting zircon ore or purified zirconia.

The titanium required by the composition which is not provided by the residues obtained from the other starting materials is supplied typically by commercially available grades of Rutile which contain at least 90% Titania and preferably in excess 95% Titania.

The requisite proportions of the major starting materials are usually pre blended with the necessary additions of carbon, usually in the form of petroleum coke or graphite, and iron. The

appropriate quantities of carbon and iron where the latter is required, can be readily calculated by those skilled in the art. Should the level of titanium fall below the required level during the fusion, additional titania may be added as necessary during the fusion to readjust the level to that required in the final product.

5 In the preferred embodiment the residual impurities in the final composition irrespective of starting materials or fusion technique employed should be kept to below the following limits. 5

Silica below 1.5 weight percent, preferably below 1.0 weight percent and ideally below 0.5 weight percent. Combined Alkali ( $\text{Na}_2\text{O}$ ) and Alkaline earths ( $\text{CaO}$  and  $\text{MgO}$ ) preferably below 1.0 weight percent and ideally below 0.5 weight percent, of which soda should comprise less than 0.1 weight percent. 10

Fusion of the selected and preblended mixture of starting materials is normally carried out in a carbon arc furnace at a temperature normally in excess of  $1800^\circ\text{C}$ .

When melted (fused), refined and adjusted with respect to titania where necessary, the fused mixture is cast or poured into a suitable cooling vehicle wherein rapid cooling and solidification of the melt takes place preferably within 1 minute desirably within 20 seconds of the molten material contacting the cooling surfaces provided by the cooling vehicle. 15

It is believed that any cooling method or vehicle may be used wherein the melted composition is cast or poured upon a heat sink having high heat conductivity, i.e. preferably in excess of about 0.05 calories per second per square centimeter per cm per degree centigrade at about  $1200^\circ\text{C}$ , and wherein the maximum distance through the cast or poured material to the nearest heat sink surface is preferably less than about 2 and more preferably less than about 0.5 centimeters. 20

Heat sink materials, such as lumps of previously solidified composition, which have lower conductivities may be used provided that the thickness of the cast or poured melted composition is substantially smaller, e.g. in the case of lumps or previously solidified material, less than 0.7 and preferably about 0.3 cm. 25

Suitable heat sink materials not only have high heat conductivity, but have reasonably high melting temperatures. Steel is a preferred heat sink material for these reasons and also because of its low cost and availability. Another example of commercially feasible heat sink material is cast iron. Examples of further possible good heat sink materials are chromium, nickel, zirconium and their alloys, although they may be too expensive for commercial use. 30

After solidification, the resulting composition is comminuted to the desired grain size and grit shape. Such comminuting is achieved using combinations of jaw crushing, impact crushing or roll crushing, i.e. Standard techniques to the industry.

The zirconia in the resulting abrasive has been usually found to be between 10 to 40% in the tetragonal crystal form. Usually the higher the residual silica level the lower the amount of the zirconia obtained in the tetragonal crystal form. 35

Overall the microstructure obtained consists of two parts;

1. Primary Alumina crystals which are embedded in,
2. a supporting Alumina Zirconia eutectic matrix.

40 The volume fraction of primary alumina crystals is about 40% at a zirconia content of 34 weight percent and about 52% by volume of primary alumina crystals when the zirconia content is 27 weight percent. 40

At the optimum eutectic composition cited in U.S. Patent 3,891,408 there would be little or no primary alumina crystals present; theoretically there would be none. At the upper limit of zirconia cited in U.S. Patent 3,891,408 of 50% by weight zirconia, the abrasive will contain primary zirconia crystals. 45 The preferred embodiment of U.S. 3,891,408, thus produces a microstructure which is predominantly pure and which consists, as far as possible, entirely of eutectic cells or colonies. 45

The microstructure of the current invention thus differs in this important respect in that it desirably contains about 40 to 52 volume percent of primary alumina crystals and must also additionally contain from 1 to 10 weight percent of Titania or a reduced form thereof. 50

The primary alumina crystals in the current invention vary in size from about 5 to 50 microns and are predominantly finer than 30 microns. Often they exhibit a dendritic type of orientated structure in which separation both between the dendrites and groups of dendrites occurs by virtue of the presence of the eutectic matrix.

55 The zirconia in the matrix exists as rods or platelets interspersed in an alumina rich background phase. The diameter of the rods or thickness of the platelets is thought to be 200—4000 Angstroms. Typically the inter rod spacing averages less than 3000 Angstroms with appreciably finer spacings existing which often cannot be clearly resolved by the scanning electron microscope. 55

The matrix consists of groups of rods or platelets of zirconia having a high degree of orientation which divide the matrix between the primary alumina crystals into a series of eutectic colonies or domains. The size of the colonies or domains typically varies between 5 and 30 microns. 60

The important or vital titania phase or a reduced form thereof, is thought to exist in solid solution with the primary alumina crystals, but it is considered that the major amount exists at the interface between the primary alumina crystals and eutectic matrix and particularly at the interface between the eutectic colonies or domains comprising the eutectic matrix in which the primary alumina crystals are 65

embedded. The other residual impurities are also thought to be located at these latter two sites where they exist individually or in combination with each other or the major phases present including the titania.

The invention will be further described by way of example only with reference to the following

#### 5 Examples.

In the examples which follow the following fusion technique and means of rapid solidification have been used.

Fusions were carried out using a 100 K.V.A. single phase fusion facility. This uses two 3" diameter graphite electrodes adjustable between 4" to 10" spacing and also adjustable with respect to height. Preblended mix of the specific composition to be examined is introduced into the case of the furnace and fusion started by laying a graphite track between the electrodes when spaced 4" apart.

Once the initial pool of molten material had been obtained additional mix was progressively added in increments and the height and spacing of the electrodes adjusted, relative to the melt, to maintain a current of 600 to 1000 amps at a voltage of 65—90 volts.

Furnacing was continued in this manner for about 30 to 40 minutes after which time the first casting was made. The electrodes were lifted above the surface of the melt and after about 2 minutes delay the molten material was poured into a mould containing 1" diameter steel balls or a Rod Mould as specified in British Patent Application No. 41763/77 having 1" diameter steel rods with a 0.19" inter rod spacing.

The quantity of material produced by each casting was about 20 to 40lbs and a number of castings were carried out for each specific composition.

The cast and solidified material produced by the above procedure was comminuted to yield abrasive grits. Typically the material was jaw crushed to yield ~ 8 grit and finer product which was then secondary roll crushed to yield a 16 grit and finer stock material. After coarse magnetizing to remove free iron contamination from the crushing equipment, the stock material was accurately sieved into cross matched grit sizes for product manufacture and physical and chemical analysis. This yielded 16 grit to 80 grit these being the most popular sizes for subsequent grinding tests. Commercially a complete grit size range would be produced.

#### Example 1

A series of such fusions were carried out in the manner described above. The starting material and mix compositions used are listed in Table No. 1.

Starting Materials		Table No. 1 Low Soda Alumina Compositions (Wt. %)					Synthetic Bauxite Compositions (Wt. %)		
		F357	F358	F359	F360	F361	F362	F363	F364
Low Soda Calcined Alumina (+99% $Al_2O_3$ ) Baddeleyite Ore (98% $ZrO_2$ ) Rutile (95% $TiO_2$ ) Silica (98% $SiO_2$ ) Ferric Oxide (87% $Fe_2O_3$ )		65.5	63.0	69.5	67.0	64.7	62.2	68.65	66.18
		32	32	28	28	32	32	28	28
		2.5	5.0	2.5	5.0	2.5	5.0	2.5	5.0
		—	—	—	—	0.6	0.58	0.64	0.62
		—	—	—	—	0.2	0.19	0.21	0.20
		100.0	100.0	100.0	100.0	100.0	99.7	100.0	100.0
Fine Graphite addition		1.0	1.2	1.0	1.2	1.0	1.2	1.0	1.2

NB: The graphite additions appear excessive but this is not the case since a large proportion is oxidised in the crust and does not enter the melt. The figures used are those found to give satisfactory results and were empirically determined on a trial and error basis. A much coarser source of carbon would appreciably reduce the quantities required.

The mix compositions in Table No. 1 after fusion, casting into a 1" Rod Mould as previously described and when solidified crushed in the manner previously indicated gave the following % chemical analyses listed in Table No. 2.

Fusion Number		Table No. 2 % Analysis						
		$ZrO_2$	$Al_2O_3$	$TiO_2$	CaO	$Fe_2O_3$	$SiO_2$	$Na_2O$
F357 F358 F359 F360		31.5	65.96	1.82	0.04	0.15	0.5	0.03
		31.2	65.07	3.35	0.01	0.05	0.3	0.02
		28.6	65.22	1.82	0.01	0.01	0.3	0.04
		29.0	65.15	3.26	0.04	0.01	0.5	0.04

Tabl No. 2 (cont.)  
% Analysis

	<i>Fusion Number</i>	<i>ZrO<sub>2</sub></i>	<i>Al<sub>2</sub>O<sub>3</sub></i>	<i>TiO<sub>2</sub></i>	<i>CaO</i>	<i>Fe<sub>2</sub>O<sub>3</sub></i>	<i>SiO<sub>2</sub></i>	<i>Na<sub>2</sub>O</i>	
5	F361	31.9	65.55	1.67	0.01	0.04	0.8	0.03	
	F362	32.0	63.73	3.28	0.04	0.01	0.9	0.04	5
	F363	29.1	68.40	1.73	0.02	0.02	0.7	0.03	
	F364	29.0	66.77	3.26	0.03	0.02	0.9	0.02	

### Example 2

10 Accurately matched grit splits in 36 grit of the compositions specified in Example 1 and produced by the methods described previously were incorporated into coated abrasive belts. A sample of conventional brown fused alumina produced by the fusion and refining of Bauxite as manufactured by The Carborundum Co. Ltd. and in the quality designated G52E which is widely used in such coated abrasive belts was also made into belts. The grit size of the G52E was accurately cross matched to the experimental compositions F357 to F364.

15 In order to eliminate variables regarding levels of dust on the different grains and possible variations in their electrostatic projection properties all grains were washed to remove the dust followed by a surface treatment to guarantee standard surface electrical conductivities.

The treated grains were then electrostatically projected onto a flexible backing material across a projection gap of about 25mm using a 19KV DC projection voltage over a time period of about 20 seconds.

20 The flexible backing material was a 4/1 sateen weave polyester cloth approximately 103x40 threads per square inch, which had previously been coated with a maker adhesive mix consisting of a commercial one stage liquid phenolic resin with a phenol to formaldehyde ratio of approximately 1:1.6 designated S363 as manufactured by The Carborundum Co. Ltd., Manchester. The S363 also contained ground limestone of an average particle size of approximately 17—25 microns. The proportion of S363 to ground limestone was 58% S363 by weight and 42% Limestone by weight. Additionally the maker adhesive also contained a wetting agent MANOXOL O.T. at a level of 0.1% by weight. The maker adhesive had a viscosity of approximately 8 poise at the coating temperature. A typical maker weight of 0.28 Kg/m<sup>2</sup> was used for 36 grit.

30 The cloth with the adhering abrasive grit at a concentration of approximately 0.9Kg/m<sup>2</sup> was then carefully dried for 1 hour (min) at 75°C, plus 3 hours minimum at 90°C.

A sizer coat is then applied to the grain surface to partially fill in the gap between the projected abrasive grits to improve their adhesion and bond strengths. The sizer weight used is approximately 0.65 Kg/m<sup>2</sup>. The composition of the sizer is basically the same as the maker adhesive but has 1½% addition by weight of PYROGENE. This prevents the sizer coat from "running" during the final drying and curing.

A typical cure after sizing is a minimum of 1 hour at 75°C and minimum 3 hours at 90°C and minimum 1 hour at 96°C and minimum 1 hour at 100°C and minimum 12 to 14 hours at 107°C.

40 After curing the product is placed in a humid atmosphere of +95% RH for 24 hours minimum. After which time the product is flexed in three directions at 45° to facilitate easy handling during the manufacture in the form of belts. Abrasive belts 82"x2" wide are made from the coated abrasive material by the usual techniques.

A series of belts incorporating the experimental abrasives F357—F364 as listed in Table No. 2 and G52E conventional fused alumina were prepared in this manner.

45 The belts produced were then evaluated on a conventional heavy duty floor backstand belt tester using mild steel workpieces in the form of rolled 3/4"x3/4"x1/8" angle cross section by about 48" long. In the test the belt is placed on the backstand in the normal manner and the workpiece so positioned so that the 3/4"x3/4"x1/8" section engages the belt just below the horizontal diameter of the contact wheel.

50 The abrasive belt is driven at 4500 surface feet per minute over a contact wheel of 14 inches in diameter. 16lbs dead weight infeed force is applied to the workpiece and 50 contacts of 2.25 seconds duration with a 10 second interval between each of the 50 contacts comprises a grinding cycle. The amount of metal removed (i.e. ground) in each grinding cycle is measured and testing is continued until the metal removed in a cycle falls to below 66gms. The total weight of material removed by the belt and the total weight lost by the belt thus define the relative performance ability of each belt when tested in this manner.

55 The abrasive belts gave the following results listed in Table No. 3.

Tabl No. 3  
1st Test Series                      2nd Test Series

Abrasive	1st Test Series		2nd Test Series		
	Metal Removed (gms)	Belt Loss (gms)	Metal Removed (gms)	Belt Loss (gms)	
5					5
F357	1888	12	1292	9.0	
F358	1265	10	1189	10.0	
F359	1470	11	1279	10.0	
F360	1848	13	Not Tested		
10 F361	1408	12	1154	10.0	10
F362	1768	19	1361	11.5	
F363	1462	12	1119	11.0	
F364	Not Tested		1267	12.0	
G52E (conventional 15 Al <sub>2</sub> O <sub>3</sub> )	571	9	415	8	15

The large performance advantage of the abrasives of the current invention over conventional fused alumina is clearly apparent. Improvements of 100 to 230% are being obtained. The difference between the two series was due to the different contact times used. Each grinding cycle of the 1st Test Series was 50 contacts of 2.25 seconds whereas each grinding cycle of the 2nd series was 50 contacts of 2 seconds duration.

#### Example 3

The test data produced for belts is obtained in what the "industry" refers to as a low cut frequency operation, i.e. the number of times each cutting point makes contact with the workpiece per second is comparatively low. Cut frequency for belts depending on the land to groove ratio of contact wheels used is typically 1 to 10 per second. In order to assess the merits of the novel abrasive compositions in high cut frequency coated abrasive applications tests were also carried out in which the abrasives were incorporated into 7" diameter coated abrasive discs. Here the cut frequency per grit can be as high as 100 per second.

Essentially the same procedures were carried out as detailed in Example 2, except that the abrasive grits were projected onto a heavy duty fibre backing material.

The maker coat for discs was a commercial one stage liquid phenolic resin with a phenol to formaldehyde ratio of 1:1.55, designated CL32 as manufactured by The Carborundum Co. Ltd. at Manchester. A 15% by weight of "Ethane Diol" is added to the CL32 and also crushed limestone in the ratio of 9 parts by weight Calcium Carbonate powder to 11 parts by weight of CL32. Wetting agent MANOXOL "OT" and water are added to give a coating viscosity of 17 poise. The maker weight used is 0.53Kg/m<sup>2</sup>. The grain weight projected electrostatically onto the maker coat is 1.4Kg/m<sup>2</sup>. (NB: Depending on the specific gravity the grain weight is modified to a constant volume basis).

The projection voltage of 19KV DC across a 25mm gap and time of 20 seconds are used. The coated product at this stage is dried for a minimum of 3 hours at 90°C.

A sizer coat is then applied which comprises:—

35% by weight of a one stage commercial liquid phenolic resin with a phenol to formaldehyde ratio of 1 to 1.6, designated CL 151 manufactured by The Carborundum Co. Ltd., Manchester, 65% by weight of Cryolite filler and in addition +2½% by weight of Denox (iron oxide pigment grade) and +0.1% MANOXOL "OT" wetting agent. The sizer weight used is about 0.69KG/m<sup>2</sup>.

The product is dried and cured for a minimum of 4 hours at 90°C plus 14—16 hours at 107°C, followed by humidification at +95% R.H. for 24 hours and ball flexed in the standard manner used in the industry. 7" diameter discs were stamped out of the coated abrasive product in the normal manner.

Accurately cross matched grit splits in 36 grit of the abrasive compositions listed in Table No. 1 and also conventional fused alumina designated G52E as indicated in Example 2, were incorporated into 7" diameter coated abrasive discs in the manner described.

The discs produced were mounted on an aluminium alloy back up pad which was faced with 1/16—1/8" thick insertion rubber. The disc was so arranged as to contact the end of a 8" diameter mild steel tube having a 1/4" wall thickness and initial length of 10 inches. The workpiece is angled vertically about 2—3° from horizontal and in the horizontal plane about 1 to 2° from normal. The workpiece rotates at 70 surface feet per minute and the disc at a peripheral velocity of 10,000 surface feet per minute. The disc is applied to the workpiece under a dead weight force of 50 pounds.

The disc grinds the workpiece for a contact period of 15 seconds after which time the workpiece is removed, weighed, watercooled and dried. Repeated contacts to this pattern are carried out until the quantity of metal removal in a 15 second contact falls below 20 gms. at which time the total metal removed and total disc loss are taken as the measure of the abrasive performance. Tests carried out in this manner on the F357—364 series and standard Alumina G52E gave the following results listed in Table No. 4.



Table No. 4

	Abrasive	Metal Removed (gms)	Disc Loss (gms)	
5	F357 } Low Soda Alumina	1004	2.73	5
	F358 }	918	2.88	
	F359 }	1071	2.80	
	F360 }	1171	4.05	
10	F361 } Synthetic Bauxite	637	1.93	10
	F362 }	735	2.68	
	F363 }	660	2.17	
	F364 }	810	2.60	
	G52E (Standard Fused $Al_2O_3$ )	537	2.20	

The abrasives of the current invention are again shown to be superior to conventional standard fused alumina G52E. Improvements upto 118% are obtained. 15

## Example No. 4

To compare the performance of abrasives of the current invention in bonded products two further fusions were carried out as described previously using the following mix compositions given in Table 5.

Table No. 5.

	Mix Composition	Fusion Numbers		
		F365	F366	
20				20
	Synthetic Bauxite Compositions			
	Low Soda Alumina $Al_2O_3$	66.7% Wt.	64.2% Wt.	
	Rutile	2.5	5.0	
	Silica	0.6	0.6	
25	Ferric Oxide	0.2	0.2	25
	Baddelyite	30.0	30.0	
		100.0	100.0	
	Fine Graphite	1.0%	1.2%	

The analyses of the abrasive grits are listed in Table 6.

	Table 6			
	F365	F366		
30				30
	$Al_2O_3$	68.72 Wt.%	65.25 Wt.%	
	$ZrO_2$	28.60	30.20	
	$TiO_2$	1.76	3.24	
35	CaO	0.04	0.02	35
	$Fe_2O_3$	0.14	0.24	
	$SiO_2$	0.76	1.08	
	$Na_2O$	<0.10	<0.10	
40	Gain on Ignition (100s and finer 1300°C for 2 hours)	0.29%	0.35%	40
	Specific Gravity	4.42 gm/cc	4.47 gm/cc	

The abrasive grits produced were accurately cross matched for shape and size distribution to a conventional fused brown alumina abrasive obtained by the fusion of Bauxite which is widely used in Bonded abrasive products and which is designated E.D.R.

## 45 Wheel Formulations

Grit splits used in the test wheels were:—

64.0%	—24+28 Mesh
36.0%	—28+32 Mesh

The bonded abrasive mix formulations used were:

		EDR	F365	F366	
	Abrasive	76.02 Wt.%	78.02 Wt.%	78.20 Wt.%	
	Bond Blend 22	17.10	15.68	15.54	
5	CS 303	1.71	1.57	1.55	5
	CL50	5.17	4.74	4.70	

NB: The different weight percentages are the adjustments made to allow for the difference Specific Gravities of F365 and F366 compared to that of EDR (which is 3.95 gms/cc). These ensure that the volume of abrasive to bonding phase is kept constant.

10 The Bond blend consists of a fine powdered mixture of CS222 resin at 36.9 wt.percent and 63.1% of a combination of whiting and potassium aluminium fluoride fillers.

The CL50 is a one stage liquid phenolic resole having a phenol formaldehyde ratio of 1:1.2. The CS303 is a powdered phenolic Novolac having a phenol formaldehyde ratio of 1:0.95. The CS222 is a powdered phenolic Novolac having a phenol formaldehyde ratio of 1:0.71.

15 The mix procedure is to wet up the grain using the CL50 and then to add the Bond blend 22 to build up the bond coating on the wetted grain. Add the CS303 as a dusting powder to complete the mix and give a free flowing mix ready for moulding.

#### Wheels

20 The above mixes were used to make Type 27 depressed centre wheels of 7" diameter and 1/4" thickness containing one internal reinforcing woven glass fabric located at the centre and one external back face reinforcing woven glass fabric. The wheels were moulded in the conventional manner to give pressed wheel densities of:—

		EDR	F365	F366	
	Hard Grade	39.5 gm/in <sup>-3</sup>	43.07 gm/in <sup>3</sup>	43.45 gm/in <sup>-3</sup>	
25	Soft Grade	38.0	41.57	41.95	25

NB: The variations in moulding density again are to allow for basic differences in abrasive specific gravities, i.e. volume of abrasive to bond in the pressed wheels are identical for a specific grade.

30 The wheels are clamped together in stacks using metal spacers shaped to the geometry of the wheels and are cured in this state. The cure cycle is approximately 27 hours up to 355°F and a soak at 355°F for 10 hours. The cured wheels are edged accurately to 7" diameter and checked for cured density prior to testing.

The type 27 depressed centre wheels of 7" diameter were tested on a machine designed specifically for evaluating this type of product.

35 The wheel is mounted in the machine which rotates the wheel at 6,000 r.p.m. The mild steel workpiece in the form of 8"x4"x1/4" thick plate is clamped beneath the wheel such that the wheel traverses backwards and forwards along the 1/4"x8" edge. The test wheel under a dead weight force of 13 lbs is presented to the workpiece at an angle typical of that used in "off-hand" grinding. There is a "rocking motion" imparted to the test piece which simulates the tilting movement used by an operator using a portable grinder. This "rocking motion" traverses the workpiece under the wheel at a rate of about 30ft minute.

40 The test involves measuring the metal removed and wheel loss incurred during 2 minutes contacts of wheel and metal. The test is continued until the metal removal obtained falls below 30 gms for a 2 minute contact. The data generated expressed the relative performance of the abrasives tested in terms of average metal removal rate, grinding ratio and quality factor. The grinding ratio is the total metal removed divided by the equivalent weight loss of the wheel. To allow for differences in wheel density due to abrasive specific gravity differences all wheel losses are standardised to the volume equivalent of standard fused alumina wheels (i.e. equivalent weight loss).

The results obtained for F365 and F366, and standard EDR fused alumina are given in Table No.

7.		Table No. 7			50	
50			Average			
			Metal Removal			
			Rate (gm/min)			
	Abrasive	Wheel Grade		G.R.	Q.F. (MRR×GR)	
55	EDR (STD Fused Alumina)	Soft	24.97	13.64	341	55
		Hard	24.86	13.05	322	
	F365	Soft	27.87	16.74	467	
		Hard	27.64	20.64	571	
	F366	Soft	27.65	20.07	555	
		Hard	27.38	27.10	742	

The data clearly shows the superior performance of the current abrasives over standard fused alumina in a bonded abrasive product. It also clearly indicates the improvement made by increasing the Titania content from 1.76% in F365 to 3.24% in F366. Performance as indicated by QF have been obtained with F366 which are up to 130% superior to standard fused alumina.

5 The above Examples have clearly demonstrated the superior low to intermediate pressure performance of abrasives of the current invention when incorporated into coated and bonded abrasive products and when compared to similar products containing conventional fused aluminas under a variety of conditions. The abrasives of the current invention gave up to 230% improvements in coated products and in excess of 100% in bonded products.

10 In order to give an indication of the performance of Alumina Zirconia eutectic abrasives containing 40—43% by weight zirconia and produced within the major claims made in U.S. Patent 3,891,408 to Rowse and Watson, performance of a commercially available Alumina Zirconia eutectic abrasive was compared with conventional fused alumina.

#### Example 5

15 When the commercially available eutectic abrasive was cross matched for grit size and shape and incorporated into coated abrasive belts as produced in Example 2 and tested as in that Example gave the results listed in Table No. 8.

Table No. 8

Abrasive	1st Test Series		2nd Test Series	
	Metal Removal (gms)	Belt Loss (gms)	Metal Removal (gms)	Belt Loss (gms)
Commercial Eutectic (40—43% ZrO <sub>2</sub> )	1699	8	1236	10
Standard G52E Conventional Fused Alumina	571	9	415	8

The performance of the eutectic abrasive was about 200% superior to conventional fused alumina.

N.B. 1st Test Series used 50 contacts of 2.25 seconds/cycle

2nd Test Series used 50 contacts of 2.0 seconds/cycle.

#### 30 Example 6

When the commercially available alumina zirconia eutectic abrasive was cross matched for grit size and shape and incorporated into coated abrasive discs as produced in Example 3 and tested as described in that Example, the results listed in Table No. 9 were obtained.

Table No. 9

Abrasive	Metal Removed (gms)	Disc Loss (gms)
Commercial Alumina Zirconia Eutectic	984	2.75
G52E Standard Fused Alumina	537	2.20

40 The commercial eutectic abrasive gave an 83% improvement when compared with standard fused alumina.

#### Example 7

45 When the commercial alumina zirconia eutectic abrasive was cross matched for grit size and shape and incorporated into Type 27 depressed centre wheel as produced in Example 4 and when tested as described in that Example the results listed in Table 10 were obtained. (NB: The specific gravity of the eutectic abrasive was accounted for in terms of mix formulations and pressed wheel densities).

Table 10

Abrasive	Wheel Grade	Average Metal Removal Rate (gm/min)	G.R.	Q.F.
Commercial Alumina Zirconia Eutectic	Soft	28.15	21.14	595
	Hard	23.70	32.19	763
Std. Fused Alumina E.D.R.	Soft	24.97	13.64	341
	Hard	24.66	13.05	322

55 The eutectic abrasive's performance is 74 to 137% superior to standard fused alumina.

The performance advantage over standard fused alumina of the commercially available alumina zirconia abrasive, embodying the major claims and teachings of U.S. Patent 3,891,408 are similar, equal or in certain instances inferior to those of the current invention. The novel and unexpected feature of the current invention was that it is produced outside the compositional limits and structural features claimed to optimise low to moderate pressure performance of the alumina zirconia system as cited in U.S. Patent 3,891,408. The ability to achieve equivalent or superior performance is made possible by the presence of the Titania or reduced form thereof. The ability to reduce the zirconia content and still maintain excellent performance can reduce raw material costs significantly.

### Claims

- 10 1. An abrasive grain comprising 27 to 35% by weight of zirconia, titanium dioxide or a reduced form thereof in an amount on analysis expressed as the oxide of 1 to 10% by weight, impurities, if any, in a total amount on analysis expressed as the oxides of not greater than 3% by weight, and a balance of alumina. 10
- 15 2. An abrasive grain as claimed in claim 1 wherein the amount of titanium dioxide or reduced form thereof is 1—5% by weight on analysis expressed as the oxide. 15
3. An abrasive grain as claimed in claim 1 or 2 wherein a reduced form of titanium dioxide is present and the reduced form is selected from a carbide, an oxycarbide or suboxide of titanium.
4. An abrasive grain as claimed in any one of claims 1 to 3 in which on analysis expressed as the oxide there is not more than 0.1% by weight of  $\text{Na}_2\text{O}$ .
- 20 5. An abrasive grain as claimed in any one of claims 1 to 4 in which on analysis expressed as the oxide there is not more than 1.5 by weight of  $\text{SiO}_2$ . 20
6. An abrasive grain as claimed in claim 5 in which on analysis expressed as the oxide there is less than 1% by weight of  $\text{SiO}_2$ .
7. An abrasive grain as claimed in claim 6 in which on analysis expressed as the oxide there is less than 0.5% by weight of  $\text{SiO}_2$ . 25
8. An abrasive grain as claimed in any one of claims 1 to 7 in which on analysis expressed as the oxides there is a total of not more than 1.5% by weight of  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$ .
9. An abrasive grain as claimed in any one of claims 1 to 8 wherein from 10—40% by weight of the zirconia is in the tetragonal crystalline form.
- 30 10. An abrasive grain comprising 27 to 35% by weight of zirconia, titanium dioxide or a reduced form thereof in an amount on analysis expressed as the oxide of 1 to 10% by weight, impurities, if any, in a total amount on analysis expressed as the oxides of not greater than 3% by weight, and a balance of alumina, said abrasive grain having a microstructure of primary alumina crystals embedded in a supporting alumina-zirconia eutectic matrix. 30
- 35 11. An abrasive grain as claimed in claim 10 wherein the primary alumina crystals have a size of 5 to 50 microns and are predominantly finer than 30 microns. 35
12. A bonded abrasive product comprising an abrasive grain as claimed in any one of claims 1 to 11.
13. A coated abrasive product comprising an abrasive grain as claimed in any one of claims 1 to 11. 40
14. A method of producing an abrasive grain as claimed in any one of claims 1 to 11 by solidification of a melt of the required composition, wherein the solidification is effected in under three minutes by contacting the melt with a suitable heat sink material.
15. A method as claimed in claim 14 wherein solidification is effected in under one minute.
- 45 16. A method as claimed in claim 15 wherein solidification is effected in under twenty seconds. 45
17. A method as claimed in any one of claims 14 to 16 wherein the heat sink material comprises metallic balls, rods or plates.
18. A method as claimed in any one of claims 14 to 16 wherein the heat sink material is lumps of previously solidified abrasive material.
- 50 19. An abrasive grain substantially as hereinbefore described in any one of the Examples. 50
20. A method of producing an abrasive grain substantially as hereinbefore described in any one of the Examples.